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Studies of Polybutenes. III. On the Molecular Motion Studied by Nuclear Magnetic Resonance*

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The molecular motion of polybutenes of low molecular weights has been studied by observing the NMR line widths and spin-lattice relaxation times at temperatures in the range from −180 to 200°C. The temperature dependence of these values is similar to that of polyisobutylene of a higher molecular weight. The correlation time spectra calculated from the spin-lattice relaxation time and the spin-spin relaxation time shift in the shorter-time direction with the decrease in the molecular weight. The dependence of the correlation frequency upon the temperature is also discussed in terms of the W. L. F. equation.

In previous papers(1,2) the molecular weight and its distribution in some polybutenes have been reported. The molecular weights from 300 to 10000 are situated between the typical high polymer and the monomer. Its chemical constituent is mainly polyisobutylene with some copolymer components of another butenes. It seems that it would be worthwhile to study the state of the molecular motion of these substances at low temperatures and to compare this motion with that of the polyisobutylene of a high molecular weight.(3)

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* Presented at the International Symposium on Nuclear Magnetic Resonance, Tokyo, September, 1965.

1) R. Endo, K. Iimura and M. Takeda, This Bulletin, **37**, 950 (1964).

2) K. Iimura, R. Endo and M. Takeda, ibid., **37**, 874 (1964).

3) J. G. Powles, *Proc. Phys. Soc.*, **B 69**, 281 (1956): J. G. Powles and K. Luszczynski, *Physica*, **25**, 455 (1959).

In the present work line-widths and spin-lattice relaxation times were observed as functions of the temperature for three samples with different molecular weights. The glass transition temperatures were determined by dilatometry. On the basis of such observations, the possible transition of the mean correlation frequency with the temperature and the distribution spectra of the correlation frequency have been discussed.

Experimental

Samples.—The samples of the commercial polybutenes used were Indopol from Amoco and Vistanex from Esso Standard. Sample A: Indopol L-10 was selected as a sample of a lower molecular weight, sample B: Indopole H-300 of a medium molecular weight, and sample C: Vistanex LM-MH of a higher molecular weight. The molecular weights of the samples A and B were determined by a cryoscopic method using benzene as a solvent. The glass-transition temperature was determined with an improved dilatometer described by Bekkedahl.[4] *n*-Propylalcohol was used as a confining liquid from −150 to 0°C.

Equipment.—The nuclear magnetic resonance spectrometer used for the line-width measurement was a JNM-BL-1 type apparatus (Japan Electron Co. Ltd.) operating at a fixed frequency of 29 Mc./s. The measurement of the spin-lattice relaxation time was carried out with a spin-echo apparatus (Japan Electron Co. Ltd.) at the resonance frequency of 25 Mc./s. by applying 90°-90° pulse method.

Results and Discussion

Table I gives the molecular weights and the glass transition temperatures for the three samples. The high-resolution nuclear magnetic resonance spectrum of sample C was identical with that of polyisobutylene. The spectrum of the sample B was very similar to that of polyisobutylene except for the appearance of weak absorptions at higher magnetic fields. These absorptions are presented to a larger extent in the spectrum of the sample A.

TABLE I. MOLECULAR WEIGHT AND GLASS TRANSITION TEMPERATURES OF POLYBUTENES

	Sample	M_w	T_g, °C
A	Indopol L-10	310	−106
B	Indopol H-300	1100	−95
C	Vistanex LM-MH	11000	−85

The Temperature Dependence of Line Widths.—The first derivative curve of the absorption spectrum was recorded for the three samples at various temperatures from −180 to 0°C. The line width at the maximum slope is plotted against the temperature in Fig. 1. The general features of these plots are similar to those of the plots observed on polyisobutylene by Powels.[3] Figure 1 shows two distinct narrowings on each curve. The low-temperature narrowing is due to the onset of a rotational motion around their three-fold axis of methyl groups. However, it may be seen that the temperature of this transition shifts lower as the molecular weight of the samples becomes smaller. This fact suggests that there is some coupling between the rotation of the methyl groups and some modes of the molecular motion of the main chain such as the rotational shear waves which have been suggested from the interpretation of the results of dynamic measurement at low temperatures. The high-temperature narrowing can be attributed to the onset of the segmental motion of these polymers. The temperatures defined as a narrowing center of the line width for samples A, B and C are −80, −54 and −38°C, respectively. The glass-transition temperatures are several tens of degrees lower than the temperatures of the narrowing center.

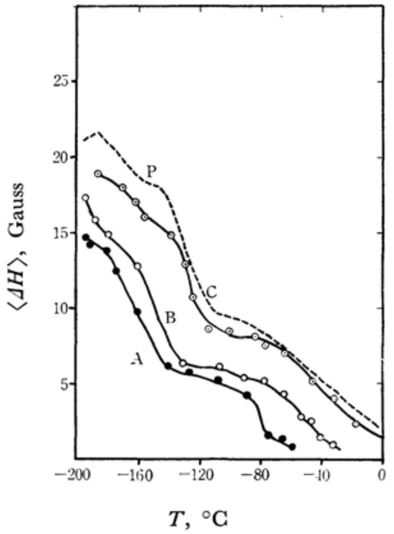

Fig. 1. Plots of line width vs. temperature.
P: data by Powles.[3]

The Temperature Dependence of the Spin-Lattice Relaxation Time. — The spin-lattice relaxation time T_1 was measured for each sample over the temperature range from −50 to 200°C. An attempt to measure the T_1 at lower temperatures was unsuccessful for the sample C. Plots of the T_1 versus $1/T$ are given in Fig. 2. Two minima have been observed in both curves concerning samples A and B. The low temperature minima are probably associated with the methyl group motion which is in turn related to the above-mentioned line-width narrowing. The high temperature minima correspond to the segmental motion. The temperatures of the T_1 minima are shifted to the lower temperature side with the

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[4] N. Bekkedahl, *J. Research Natl. Bur. Standard*, **42**, 145 (1949).

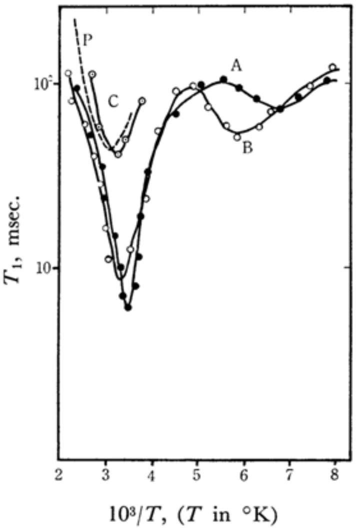

Fig. 2. Spin-lattice relaxation time as a function of temperature.

decrease in the molecular weight. The results of all the samples obtained are summarized in Table II.

TABLE II. TEMPERATURES AND VALUES OF T_1 MINIMA

Sample	T, °C	T_1, msec.	T, °C	T_1, msec.
A	12	6.4	−120	73.2
B	19	8.3	−90	65.4
C	44	42	—	—

The Temperature Dependence of the Correlation Frequency and Its Distribution.—

The motional effects of the spin-lattice relaxation time T_1 and the spin-spin relaxation time T_2 for a coupling of nuclei were interpreted by the following equations:⁵⁾

$$1/T_1 = 2/3 \cdot \varDelta\omega_2{}^2\{\tau/(1+\omega^2\tau^2)+4\tau/(1+\omega^2\tau^2)\}$$

$$1/T_2 = \varDelta\omega_2 \cdot 1/\alpha \cdot \tan^{-1}(\alpha\tau/T_2)$$

where α is the numerical coefficient nearly equal to unity and $\varDelta\omega_2{}^2$ is the second moment in units of angular frequency. In the case of the polymers, however, a simple application of the above equations does not give a reasonable temperature dependence of the correlation frequency. One of the main reasons for this may be the neglect of the distribution of correlation frequencies. It is often necessary to postulate the distribution in order to explain the dynamic and dielectric behavior of the polymer. As the values of T_1 and T_2 as a function of the temperature were obtained from measurements at a fixed frequency, it is impossible to get the distribution from the isochronal NMR data alone. Therefore, we have to reduce the data of the temperature dependence to those of frequency dependence in some way. In dynamic and dielectric studies the relation between the frequency and the temperature can be explained by the W. L. F. equation which is widely used in discussing the segmental motion of the amorphous polymers. Slichter and Davis⁶⁾ have shown on the basis of their observation of the frequency dependence of the $T_{1\,\mathrm{min}}$ value for natural rubber, that the relation between the frequency and the temperature in the spin-lattice relaxation process can be explained by the W. L. F. equation. The shift factor which relates the correlation frequency at the temperature T with that at the reference temperature T_s can be expressed by the form:

$$\begin{aligned}\log a(T) &= \log\{\tau(T)/\tau(T_s)\}\\ &= -8.86(T-T_s)/101.6+T-T_s\end{aligned}$$

where T_s is chosen 50°C higher than the glass-transition temperature. In Fig. 3, the smooth curves passing through the point of each T_2 show the temperature dependence of the correlation frequency using the shift factor. It may be seen that the application of the W. L. F. equation can not describe this case completely since all the ν_c points at $T_{1\,\mathrm{min}}$ appear somewhat below each curve. However, that equation can be used for most practical purposes.

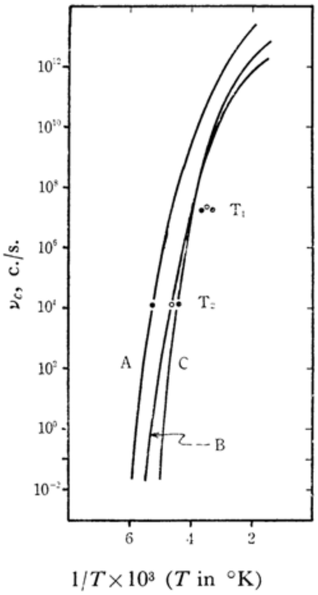

Fig. 3. Correlation frequencies as a function of temperature.

It has been proposed by Miyake⁷⁾ that the correlation-time spectra can be obtained from the

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5) R. Kubo and K. Tomita, *J. Phys. Soc. Japan*, **9**, 888 (1954).

6) W. P. Slichter and D. D. Davis, *J. Appl. Phys.*, **34**, 98 (1963).

7) A. Miyake, *Rep. Prog. Poly. Phys. Japan*, **4**, 36 (1961).

observed values of T_1 and T_2 as a function of the temperature when the W. L. F. equation is applicable to the case of nuclear magnetic resonance. According to his method the correlation time spectra calculated from the observed values of T_1 and T_2 are shown in Fig. 5 using the following equation:

$$I\{\sqrt{1/2}\,\omega_0 a(T)\} \simeq 0.733\omega_0/\Delta\omega_2{}^2 T_1$$

$$I\{T_2/a(T)\} \simeq 4.60(T_2{}^\circ/T_2) \times \{1-\mathrm{d}\log a(T)/\mathrm{d}\log T_2\}^{-1}$$

in which $T_2{}^\circ$ is the particular value of T_2 when the temperature is sufficiently low and no motional narrowing is observed. It may be seen that the correlation time spectra for T_1 in Fig. 4 are slightly affected by the molecular weight while those of T_2 in Fig. 5 depend very much on the molecular weight. The dependence of the correlation-time spectra upon the molecular wieght seems to suggest that not only the micro-brownian motion but also the macro-brownian motion may be related to the distribution spectrum. This seems to be consistent with the fact that the curve of T_1 vs. $1/T$ in the sample A has a sharper and deeper minimum than in the sample C, and that the glass-transition temperature increases with the increase in the molecular weight.

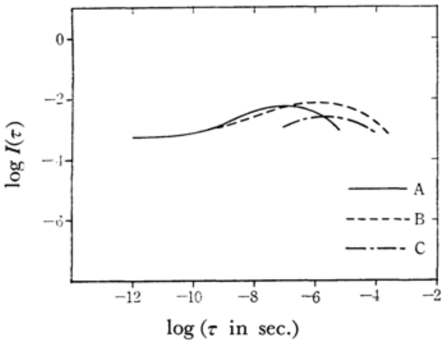

Fig. 4. Correlation time spectra calculated from spin-lattice relaxation time.

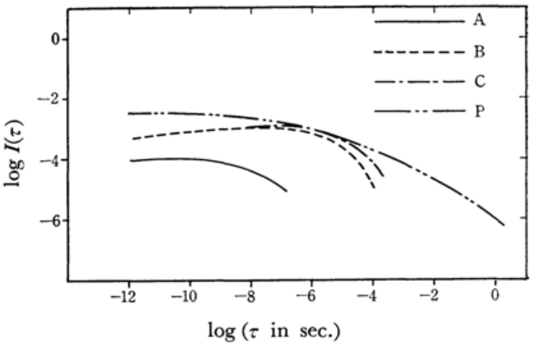

Fig. 5. Correlation time spectra calculated from spin-spin relaxation time.

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